Enclosure 3

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	12/03/2001	Final Report 6/01/98-11/30/01

4. TITLE AND SUBTITLE
Solid State Formation and Properties of Bulk Amorphous and Nanocrystalline Refractory Metal-Based Alloys

5. FUNDING NUMBERS
Contract DAAG55-98-1-0087

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8. PERFORMING ORGANIZATION REPORT NUMBER
~~P-37395-MS~~

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U. S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

37395.8-MS

11. SUPPLEMENTARY NOTES

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13. ABSTRACT (Maximum 200 words)

The goals of our research are to understand solid-state amorphoization that accompanies the early stages of phase separation in multinary titanium-based alloys, to apply the concept of solid-state amorphization to other bulk alloys, and to study bulk-glass formability and devitrification in aluminum-based alloys. State-of-the-art electron microscopy, x-ray diffraction, and differential scanning calorimetry are utilized to perform the research.

Effects on glass formability due to atomic size and interaction factors have been studied. Influence of the latter on the liquidus temperature of multi-component alloys and subsequently the overall effects on glass formability are investigated. Several phase diagrams of multinary aluminum-based alloys that exhibit deep-eutectics have been identified. Meanwhile, devitrification studies have been performed using detailed thermal and microstructural characterization. New results on the crystallization of aluminum-glasses have revealed the tendency toward forming nanoscale aluminum-rich clusters in the liquid state in the most easily formed aluminum-glasses. Currently, a semi-quantitative algorithm based on knowledge about binary and ternary systems is being developed to facilitate the screening of multinary alloys. Toward the end of our current ARO funding period, we have begun to extend the work to include aluminum-magnesium base multinary alloys.

14. SUBJECT TERMS	15. NUMBER OF PAGES
	5
	16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT	18. SECURITY CLASSIFICATION ON THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
Prescribed by ANSI Std. 239-18
298-102

20020125 248

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SUBMITTED FOR PUBLICATION TO (applicable only if report is manuscript):

Sincerely,
Joseph Poon

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List of Publications

K.J. Doherty, "Investigation of Early-Stage Spinodal Decompositions in Ti-Cr-Cu-Fe-Mn and Ti-Cr Alloys", doctoral thesis, University of Virginia (1999).

F.Q. Guo, S.J. Poon, and G.J. Shiflet, "Investigation of Glass Formability in Al-Based Multinary Alloys", Scripta Mater. 43, 1089 (2000).

F.Q. Guo, S.J. Poon, and G.J. Shiflet, "Glass Formability in Al-Based Multinary Alloys", Materials Science Forum, 331-337, 31 (2000).

F.Q. Guo, S. Enouf, S.J. Poon, and G.J. Shiflet, "Role of Atomic Size on Glass Formability and Thermal Stability of Al-Based Amorphous Alloys", Materials Transactions, JIM 41, 1406 (2000).

F.Q. Guo, S. Enouf, S.J. Poon, and G.J. Shiflet, "Formation of Ductile Al-Based Metallic Glasses Without Rare-Earth Elements", Phil. Mag. Lett. 81, 203 (2001).

F.Q. Guo, S. Enouf, S.J. Poon, and G.J. Shiflet, "Two-Step Precipitation of Alpha-Al in Al-Ni-Gd Metallic Glasses", to be submitted to recognized scientific journal.

F.Q. Guo, S.J. Poon, and G.J. Shiflet, "Studies of Glass Formability in Multinary Alloys Based on Mg-Al", in preparation.

Scientific Personnel

S. Joseph Poon - Principal investigator

Gary J. Shiflet - Principal investigator

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Sebastien Enouf - Part-time graduate research assistant

Report of Invention

None

Scientific Progress and Accomplishments

(1) Study of solid-state amorphization and spinodal decomposition -

Attempts were made to enhance the amorphization of Ti-Cr-Cu-Mn-Fe alloys with the addition of beryllium. Beryllium was selected in view of the low eutectic temperature exhibited in the Ti-Be system. However, we were only able to add Be in small amounts (up to 3 at. %) to the host alloys and still be able to achieve a single bcc phase upon quenching. Be behaves in a similar manner to copper and has an even stronger tendency in encouraging phase separation instead of causing strain in the matrix which was found to result in solid-state amorphization. For these reasons, we were unable to improve on the bulk amorphization behavior of Ti65Cr13Cu16Mn4Fe2. Thus, the effects of Be on glass formability are completely different for Zr and Ti alloys.

In order to gain a better understanding of the early stages of the phase separation that accompanies the formation of nanoscale amorphous regions in $Ti_{65}Cr_{13}Cu_{16}Mn_4Fe_2$, the binary Ti-Cr was reexamined. The latter was first reported to exhibit bulk solid-state amorphization more than a decade ago. There have always been inconsistencies in the description of the mechanism of decomposition of the beta phase in titanium alloys aged at low temperatures. We used analytical electron microscopy to show the difference in mechanism of the phase separation occurring in Ti60Cr40. Nucleation and growth of two different bcc phases occurred during aging at 550°C; spinodal decomposition was the active mechanism while aging at 400°C. These results have substantiated the existence of the spinodal and coherent spinodal in the Ti-Cr system. In addition, these findings have also validated spinodal decomposition in Ti65Cr13Cu16Mn4Fe2 and establish analytical electron microscopy as a successful method in chemically characterizing decomposition reactions.

(2) Investigation of glass formability in high-order Al-alloys -

Aluminum glasses are unique in that they do not follow the empirical rules on glass formation ability (GFA). We have evaluated the relationship between the GFA and some GFA related parameters in ternary Al-Ni-Gd as well as multinary alloys based on the ternary system. A wide range of elemental substitutions that include B, P, Si, Ge, Ga, Y, Zr, Fe, and Co are involved. In our experiment, an alloy is said to have high GFA if melt-spun glassy ribbons up to ~0.2-0.3 mm can be made. It is found that those alloys that are expected to have the best GFA in view of the higher thermal stability of the amorphous phase, higher reduced glass temperature, and higher viscosity of the melts exhibit lower GFA than those that possess apparently less favorable GFA criteria. Based on our results, the increased solidification range, defined as the temperature difference between the eutectic and final melting reactions, is suggested to be responsible for the decreased GFA of alloys. We also obtain evidence that rare earth (RE) elements play a more important role than transition metals (TM) in the GFA. The high GFA despite the existence of a large solidification range underscores the importance of strong Al-TM and Al-RE bonds.

Our strategy to explore bulk glass formation in Al-alloys will be to combine the concept of low eutectic temperature and with the idea of strongly hybridized electronic orbitals. We have continued to investigate the phase diagrams of multinary Al-alloys based on knowledge of binary and ternary phase diagrams. Several findings are presented.

Based on the relationships between the "solidification temperature range" and atomic interaction, we have studied multinary alloys starting with several ternary systems Al-Cu-Mg, Al-Cu-Ge, and Al-Cu-Si that exhibit a low liquidus temperature (~450-500°C). "Strong" elements are added to the ternary systems for evaluating the interplay of liquidus temperature and atomic size and interaction. It is found that a fully amorphous phase can be formed by adding 2-8 at.% Ni, Pd, Fe, and Co, but not the rare-earth and alkaline-earth elements, to the host ternary systems. The amorphicity is confirmed by x-ray and electron diffraction as well as DSC scans. Thermal

analysis has provided evidence for a nucleation and growth process during isothermal devitrification. A rather high tensile strength of ~800-900 MPa is measured. The liquidus temperatures of these new multinary alloys (~600C), though higher than that of the host systems, are lower than that of Al-TM-Ln (~850-900C), which suggests that upon increasing the glass temperature more stable glasses could be discovered. Good GFA is now being explored in the new multinary systems. The Al-Cu-Mg based glasses will also provide a new system for further atomistic determination of aluminum-glasses. Meanwhile, we are also investigating why amorphization has failed in alloys where the atomic size and interaction factors are apparently favorable for easy GF.

In another set of multinary alloys, alkaline-earth elements Ca, Sr, and Ba with larger atom size and strong atomic interaction are substituted for Gd. The additions do add to the stability, but not the GFA. In fact, the maximum amorphous sample thickness is found to decrease as the rare-earth content increases. Clearly these findings, together with those mentioned above, seem to underline the importance of structural determination for evaluating the atomistic network, specifically the "packing efficiency" of the amorphous structure.

Summing up the above findings, it is suggested that the distribution of atomistic interaction and packing of atomic species are important for GFA.

(3) Precipitation of alpha-Al during devitrification –

In view of the appearance of a prepeak in the devitrification of Al-glasses with the highest GFA, we have performed systematic studies of the crystallization using XRD, DSC, TEM, and HRTEM techniques. It is found that alpha-Al crystallizes in two steps, namely during both the primary as well as secondary devitrifications. However, depending upon the Al content, a clear glass transition (Figure 1) followed by a nucleation-and-growth process just prior to the 1st devitrification is observed only in the lower-Al alloys (≤86 at.%). In contrast, a nucleation-and-growth process, which results in the formation of alpha-Al, is observed prior to the 2nd devitrification peak, irrespective of the Al content (Figure 2, the lower-Al exhibit similar x-ray patterns and are thus not shown). After the 3rd devitrification peak, the phase Al_3Gd emerges. It is proposed that the 2nd–stage devtirfication involves a homogeneous nucleation process in all the alloys. While for the 1st-stage reaction, it has to do with the size of the Al-aggregates, or embryos, in the liquid state. For the lower-Al alloys, the embryos are sub-critical, while for the higher-Al alloys the embryos have almost reached the critical size. However, despite the tendency in forming Al embryos in the liquid state, thick samples of up to 0.3 mm can be made. This peculiar aspect of GFA in Al-glasses is not understood at present.

(4) Investigation of Glassy Formability in *Mg-Al* Hybrid Multinary Alloys –

Since September, we have started to investigate GFA in Mg-Al base alloys. Upon exploring Mg-Al hybrid alloys that also contain noble metals and elements with atomic radii large than Al and Mg, we have obtained new metallic glasses that exhibit quite large crystallization temperatures in the range 250-380C. Further alloying effort under the auspices of DARPA will focus on obtaining bulk amorphous and nanocrystalline Mg-Al hybrid alloys.

Technical Transfer

None

Technical Report Since all technical information has been reported either in the form of manuscripts to be submitted for publication or reprints of publications in archival journals, thus Technical Report will not be submitted with this Interim Report. Reprints, as soon as they are available, will be sent the ARO.

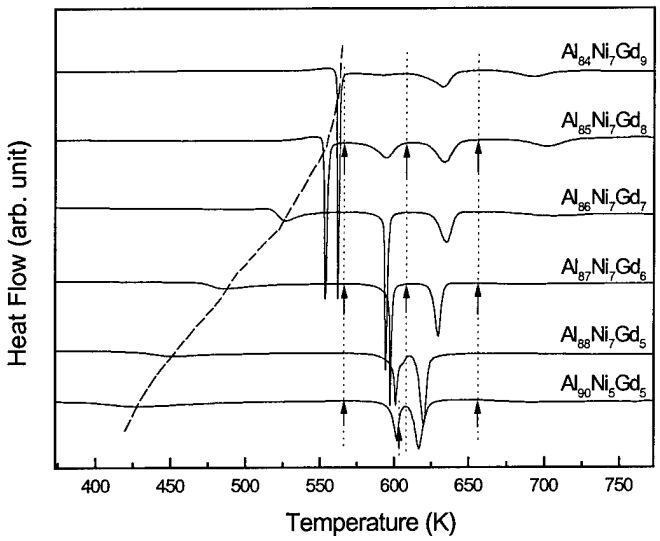

Figure 1

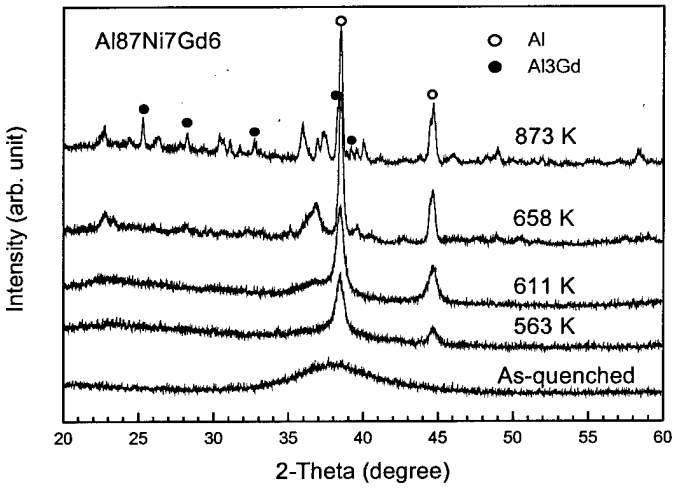

Figure 2